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OF MIXED ACIDIC AND BASIC POLYMERS

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OSMOTIC PRESSURE STUDIES OF NON-AQUEOUS SOLUTIONS
OF MIXED ACIDIC AND BASIC POLYMERS

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INTRODUCTION

Studies of the solution properties of polymers are generally concerned with the elucidation of the size and shape of the isolated macromolecules and with the interaction of these molecules in solutions of finite concentration. A suitable extrapolation to infinite dilution of such functions as reduced viscosity or reduced osmotic pressure supplies information of the first type, while the concentration dependence of these functions can be interpreted in terms of molecular interaction. If the solvent medium or the temperature is changed, the extent of aggregation of the polymer will be affected, but since the forces between polymer segments belonging to different macromolecules are the same as those between segments of any one chain molecule, such changes will alter both the interaction parameters and the parameters characterizing the isolated polymer molecule.

An attempt at a new approach to the study of polymer interactions has recently been reported from this laboratory.⁽¹⁾ Instead of studying the solution behavior of a single polymer, solutions of mixtures of two polymers similar except for the presence of a few acidic and basic groups respectively were investigated. Thus it was possible to vary the extent of polymer-polymer interaction in a constant solvent medium at constant temperature by varying the ratio of the two polymers in solution. Solution viscosity studies showed that the slopes of reduced viscosity-concentration plots increased sharply with an increase in the number of interacting groups. The intrinsic viscosities of the mixed polymers, on the other hand, were normal, indicating that the effect of polymer association is eliminated by the usual extrapolation procedure.

It has been reported that the molecular weights of certain polymers, as calculated from the reduced osmotic pressure extrapolated to infinite dilution, vary with temperature or the solvent medium⁽²⁾⁽³⁾. This behavior is apparently due to the formation of relatively stable association complexes of the polymer molecules, which may be due to a tendency of the polymer to form microcrystallites,⁽²⁾ to the presence of polar catalyst residues in non-polar polymers⁽³⁾ or a non-polar co-monomer in a hydrophilic polymer⁽⁴⁾. By measuring osmotic pressures of solutions of mixed acidic and basic polymers with known concentrations of interacting groups, in different solvents and at different temperatures, a systematic study of such association phenomena can be carried out. In the present investigation copolymers of methyl methacrylate with methacrylic acid and di-ethylamino ethyl methacrylate, respectively, were used. These systems were chosen because of the similar reactivity characteristics of the monomers, so that copolymerization could be carried to fairly high conversion without danger of an appreciable drift in the composition of the copolymer.

MATERIALS AND PROCEDURE

Monomers and polymerization catalyst

Methyl methacrylate (Rohm and Haas Co.) was distilled under nitrogen at a pressure of 3.5 mm. Hg., collecting the material within the boiling range of 17°C-18°C.

Glacial methacrylic acid (Rohm and Haas Co.) was distilled under nitrogen at a pressure of 20 mm. Hg., (b.p. 70°C.).

Dimethylamino ethyl methacrylate (Monomer-Polymer, Inc.) was distilled after addition of 0.2% picric acid inhibitor. The boiling range was 55.5°C.-56.5°C. at 3.5 mm. Hg.

Azo-bis-isobutyronitrile obtained from the Eastman Kodak Co. was used without further purification.

Preparation of copolymers

Copolymer A was prepared by heating 361 gms. methyl methacrylate, 16.4 gms. methacrylic acid, 361 gms. benzene and 0.722 gms. azo-bis-isobutyronitrile catalyst for 6½ hours at 60°C. The reactants were shaken every hour. The polymer solution was diluted with 3000 ml. butanone and precipitated into a seven-fold excess of hexane. The polymer was purified by reprecipitation from a 3% butanone solution into a ten-fold excess of hexane and dried in vacuo at 40°C. The yield was 173 gms. (46% conversion).

Copolymer B was prepared from 295 gms. methyl methacrylate, 24.4 gms. dimethylamino ethyl methacrylate, 0.59 gms. azo-bis-isobutyronitrile and 295 gms. benzene. The polymerization and polymer purification were carried out in the same manner as with copolymer A. The yield was 143 gms. (45% conversion).

Analysis of copolymers

The copolymers were analyzed by titration of 0.5% solutions in a benzene-ethanol mixture containing 90% by volume of benzene. Sodium ethoxide in the same solvent mixture and phenolphthalein indicator were used to determine the carboxyl content of copolymer A. Nitrogen was passed through

the solution during the titration. The sodium ethoxide solution was standardized against benzoic acid in the same solvent medium. A solution of HCl in the benzene-ethanol mixture (prepared by adding 0.05 ml. 12N aqueous HCl to 100 ml. of the mixed solvents) was used to titrate the amine in copolymer B. Methyl orange indicator was used and the titrating solution was standardized against sodium ethoxide.

Copolymer A was found to contain 4.9 ± 0.07 mol % methacrylic acid, copolymer B contained 5.83 ± 0.07 mol % of dimethyl amino ethyl methacrylate. This compared with 5 mol % of the acidic and basic co-monomer respectively in the mixed monomers.

Osmotic pressure measurement

Technical butanone was dried over night over anhydrous calcium chloride, filtered and distilled. The medium fraction boiling at 79.6°C . was collected.

Benzene and pyridine (Mallinckrodt analytical reagent grade) were similarly dried and distilled. Wet regenerated cellophane film membranes type 300 obtained from Sylvania Division, American Viscose Company were used after conditioning to the appropriate solvent.

Zimm-Hyersson osmometers having stainless steel plates were employed. Temperature fluctuations of the thermostatic bath used for the measurements were less than 0.005°C . Osmotic equilibrium was attained within 1-3 days for all solutions containing an excess of basic polymer whereas equilibrium was approached progressively more slowly for solutions containing an increasing excess of acidic polymer in benzene or butanone. For the pure acidic polymer in butanone, the osmotic pressure increased continuously for about 20 days.

This slow approach to equilibrium was not caused by the slowness of the diffusion process through the membrane since attempts to raise the solution level in the osmometer were followed by a rapid drop of this level, followed by a slow rise as if there had been no interference. By contrast, osmotic equilibrium with pyridine solutions of the acidic polymer were reached very rapidly (about 3 hours). In this case there was considerable diffusion of the polymer through the membrane which had to be allowed for by a suitable extrapolation to zero time.

Since benzene solutions containing mixtures of the acidic and basic copolymers tend to gel below 45°C., special precautions had to be observed in preparing the solution and filling the osmometers.

The slopes and intercepts of the reduced osmotic pressure plots were calculated by the least squares method.

RESULTS AND DISCUSSION

The reduced osmotic pressures of solutions of the copolymers A and B and their mixtures in butanone at 30.2°C. and 50.1°C, and in benzene at 49.7°C. are plotted in Figures 1,2,3,4,5 and 6. In all cases the reduced osmotic pressure is a linear function of concentration, the slope changing gradually from the slightly positive value of copolymer B to the slightly negative slope of copolymer A. It appears, that this slope is linear in the weight composition of the mixture (Figure 7).

The molecular weights of the basic copolymer calculated from the intercepts of the reduced osmotic pressure plots in the two solvents checked within the experimental error (135,000 and 134,000 in butanone at 30.2°C.

and 50.1°C. respectively and 137,000 in benzene). By contrast, the acid copolymer showed strong association in benzene at 49.7°C. with an apparent molecular weight of 184,000 as against values of 42,200 and 34,000 obtained from the osmotic pressures in butanone at 30.2°C. and 50.1°C. respectively. To eliminate the uncertainty as to the true molecular weight of the acid copolymer, osmotic pressures were determined in pyridine at 49.7°C. In this basic solvent carboxyl association is unlikely and the molecular weight obtained was 32,300.

On extrapolating the reduced osmotic pressures of the mixed copolymers to zero concentrations, very low values were obtained, which in most cases were actually lower than those of either component of the mixture. Since all polymer aggregates must necessarily dissociate at infinite dilution, the results indicate that this dissociation becomes appreciable only in solutions too dilute for osmotic pressure measurement. In Figure 8, the reciprocal apparent number average molecular weights ($1/\bar{M}_n$) calculated from the reduced osmotic pressure intercepts are given as a function of the weight composition of the copolymer mixture. If there is no association between the components of a mixture, the reciprocal number average molecular weight is linear in the weight composition and the dashed line in Figure 8 represents the $1/\bar{M}_n$ values corresponding to the absence of molecular aggregation. We may define a "degree of association" D as the ratio of the apparent molecular weight found experimentally to the value which would result on dissociation of all polymer complexes. This quantity D represents the average number of polymer molecules forming one kinetic unit and it is given as a function of the

weight composition of the copolymer mixtures in Figure 9. It can be seen that in butanone the number of polymer molecules forming an aggregate increases steeply on mixing the two copolymers, sharp maxima of $D = 5.43$ and $D = 3.20$ being obtained for a mixture of equal weights of the two components at 30.2°C . and 50.1°C . respectively. In benzene, the results indicate that acid-base interaction is superimposed on strong carboxyl association. A published study of ternary systems containing benzene, low molecular weight carboxylic acids (A) and tertiary amines (N) indicated⁽⁵⁾ the presence of complexes of the type NA_2 and NA_4 in addition to NA and A_2 and similar equilibria exist probably in solutions of the mixed copolymers in benzene.

A thermodynamic treatment of the results is given in the Appendix. If the ideal state of the copolymer A is that of a hypothetical solution of the same composition from which polymer association is eliminated, then its activity coefficient in presence of such association is

$$\gamma_A = f(\alpha_A) \beta_A^c \quad (1)$$

$$\ln \beta_A = - \frac{M_A}{M_B} \left(\frac{1 - \alpha_A}{D} \right)^2 \left(\frac{dD}{d\alpha_A} + \frac{1}{D} - 1 \right) \quad (2)$$

where M_A and M_B are the molecular weights of the two polymer species, α_A is the weight fraction of copolymer A in the polymer mixture and c is the total polymer concentration. The function $f(\alpha_A)$ is unknown, since the osmotic pressures in the concentration range in which the polymer aggregates dissociate and approach ideal solution behavior, are too small to be

measurable. As a result, only relative activity coefficients can be calculated. An analogous expression holds for activity coefficients of the basic copolymer. Values of β_A and β_B for butanone solutions at 50.1°C. are plotted in Figure 10. In these solutions the interpretation of the results is simplified by the virtual absence of any association of the acidic copolymer. The activities of the two polymers are given by

$$\begin{aligned} a_A &= c \gamma_A = f(\alpha_A) c^{1+\beta_A} \\ a_B &= c \gamma_B = f(\alpha_B) c^{1+\beta_B} \end{aligned} \quad (3)$$

so that in the composition range in which β_A or β_B is smaller than -1, the activity of the corresponding polymer species decreases with increasing concentration. We believe that an effect of this kind has not previously been observed.

Since this study was exploratory in nature, unfractionated polymer samples were used. It has been reported⁽³⁾ that the degree of association of polymers which tend to aggregate increases with the molecular weight of the polymer fraction and this observation should be checked with polymers having known concentrations of interacting groups.

The authors are grateful to Mr. L. S. Yang and Mr. M. Silberberg for the preparation and analysis of the copolymers used in this work.

APPENDIX: Activity Coefficients of Acidic and Basic Polymers in Solutions of their Mixtures.

Consider a ternary system containing a solvent (denoted by subscript o) and two interacting polymers, A and B. Through osmotic pressure measurements, the partial molar free energy of the solvent $\overline{\Delta F}_o$ is known as a function of the composition of the system. From these $\overline{\Delta F}_o$ values we want to derive values of partial molar free energies of the polymer components. Denoting by n the number of moles of the components, M their molecular weights and ρ their densities, we have for a constant total volume of the solution V

$$\left(\frac{d\overline{\Delta F}_o}{dn_A} \right)_{n_B V} = \frac{\partial \overline{\Delta F}_o}{\partial n_o} \frac{dn_o}{dn_A} + \frac{\partial \overline{\Delta F}_o}{\partial n_A} = - \frac{\partial \overline{\Delta F}_o}{\partial n_o} \frac{M_A \rho_o}{M_o \rho_A} + \frac{\partial \overline{\Delta F}_o}{\partial n_A} \quad (4)$$

For dilute solutions the concentration of polymer A is approximately

$$c_A = n_A M_A \rho_o / n_o M_o \text{ and}$$

$$\left(\frac{d\overline{\Delta F}_o}{dc_A} \right)_{c_B V} = \frac{M_A \rho_o}{M_o n_o} \left(1 + \frac{c_A}{\rho_A} \right) = \frac{c_A M_A \rho_o}{n_o M_o \rho_A} \frac{\partial \overline{\Delta F}_o}{\partial c} + \frac{\partial \overline{\Delta F}_o}{\partial n_A} = \frac{c M_A \rho_o}{n_o M_o \rho_A} \frac{\partial \overline{\Delta F}_o}{\partial c} - \frac{c}{n_o} \frac{\partial \overline{\Delta F}_A}{\partial c} \quad (5)$$

where c is the total concentration of the mixed polymers.

Since $\overline{\Delta F}_o$ is related to osmotic pressure by $\overline{\Delta F}_o = \pi \overline{V}_o \times \pi M_o / \rho_o$, and c_A / ρ_A is small compared to unity,

$$\frac{\partial \overline{\Delta F}_A}{\partial c} = M_A \left\{ \frac{1}{c} \left(\frac{\partial \pi}{\partial c_A} \right)_{c_B V} - \frac{1}{\rho_A} \frac{\partial \pi}{\partial c} \right\}$$

All experimental results in this study conformed to a concentration dependence of osmotic pressure of the form $\pi = Xc + Yc^2$ where X and Y were

functions of $\alpha_A = c_A/c$, the weight fraction of polymer A in the mixed polymer. Thus

$$\frac{\partial \bar{\Delta F}_A}{\partial c} = M_A \left\{ \frac{c_B}{c^2} \frac{dX}{d\alpha_A} + \frac{X}{c} + \frac{c_B}{c^2} \frac{dY}{d\alpha_A} + 2Y - \frac{X}{\rho_A} - \frac{2Yc}{\rho_A} \right\} \quad (7)$$

If we define the activity coefficient of polymer A by $\gamma_A = a_A/a_A^*$, where a_A is the actual activity and a_A^* the activity that would result in the absence of specific interactions between the polymers, then

$$\bar{\Delta F}_A - \bar{\Delta F}_A^* = RT \ln \gamma_A \quad (8)$$

In the absence of specific interactions the intercept of the reduced osmotic pressure plot of a mixed polymer is $X = \alpha_A \frac{RT}{M_A} + (1-\alpha_A) \frac{RT}{M_B}$

and $dX/d\alpha_A = \frac{RT}{M_A} - \frac{RT}{M_B}$. Since the second virial coefficient Y appears to be unaffected by the acid-base interaction of the polymers,

$$\frac{\partial}{\partial c} (\bar{\Delta F}_A - \bar{\Delta F}_A^*) = RT \frac{\partial \ln \gamma_A}{\partial c} = M_A \left\{ \frac{c_B}{c^2} \left(\frac{dX}{d\alpha_A} + \frac{RT}{M_B} - \frac{RT}{M_A} \right) + \left(1 - \frac{c_B}{c} \frac{RT}{M_B} - \frac{c_A}{c} \frac{RT}{M_A} \right) \left(\frac{1}{c} - \frac{1}{\rho_A} \right) \right\} \quad (9)$$

and since $\frac{1}{\rho_A} \ll \frac{1}{c}$

$$\frac{\partial \ln \gamma_A}{\partial c} = \frac{M_A}{RTc} \left\{ (1-\alpha_A) \frac{dX}{d\alpha_A} + X - \frac{RT}{M_A} \right\} \quad (10)$$

and in terms of the "degree of association D" defined by

$$D = \frac{1}{X} \left\{ (1-\alpha_A) \frac{RT}{M_B} + \alpha_A \frac{RT}{M_A} \right\} \quad (11)$$

we obtain

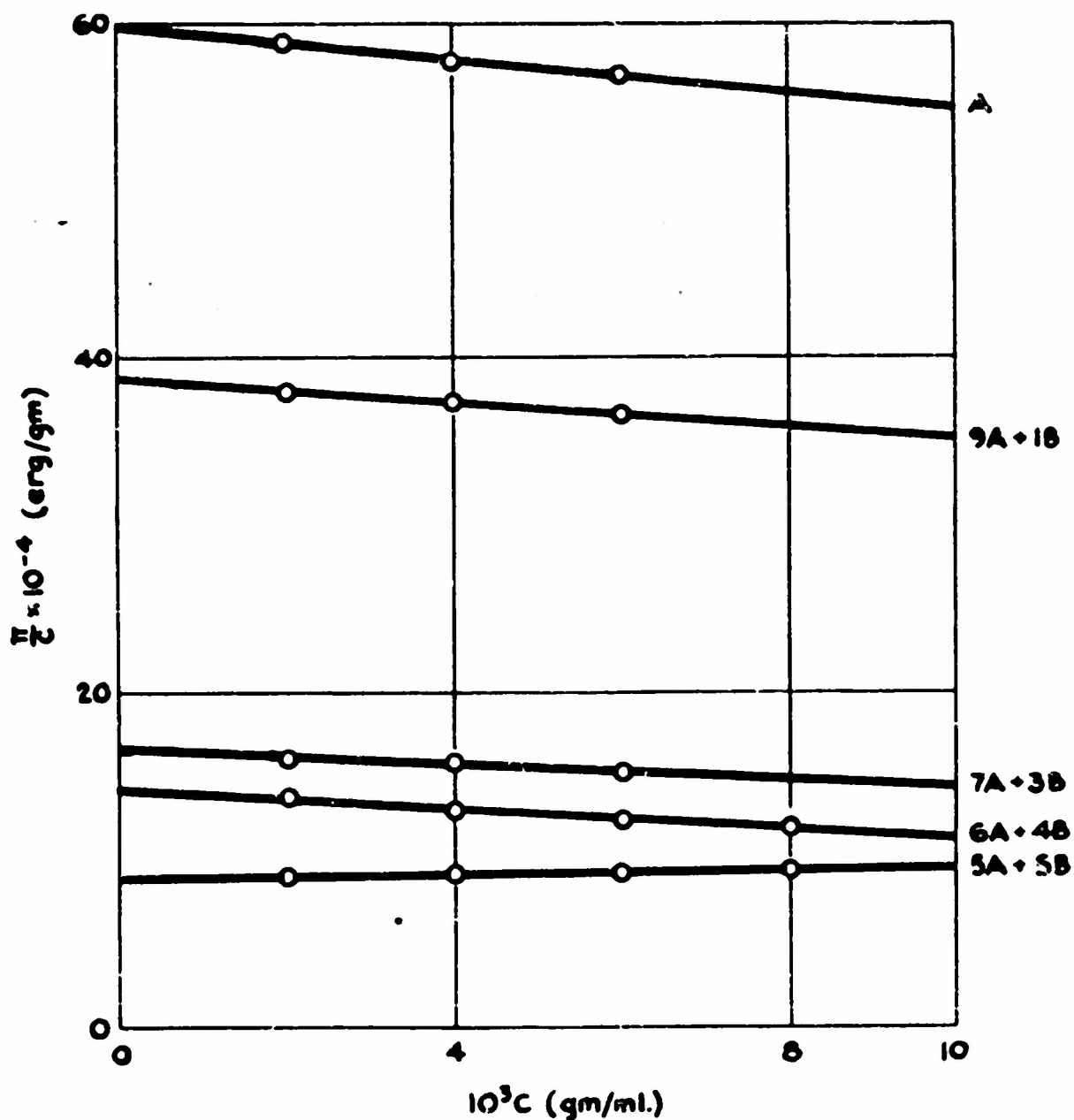
$$\frac{(\partial_A)c'}{(\partial_A)c} = \left(-\frac{M_A}{M_B} \left(\frac{1-\alpha_A}{D} \right)^2 \frac{dD}{d\alpha_A} + \frac{1}{D} - 1 \right) \ln \frac{c'}{c} + \beta_A \ln \frac{c'}{c} \quad (12)$$

$$\gamma_A = f(\alpha_A) c^{\beta_A} \quad (13)$$

References

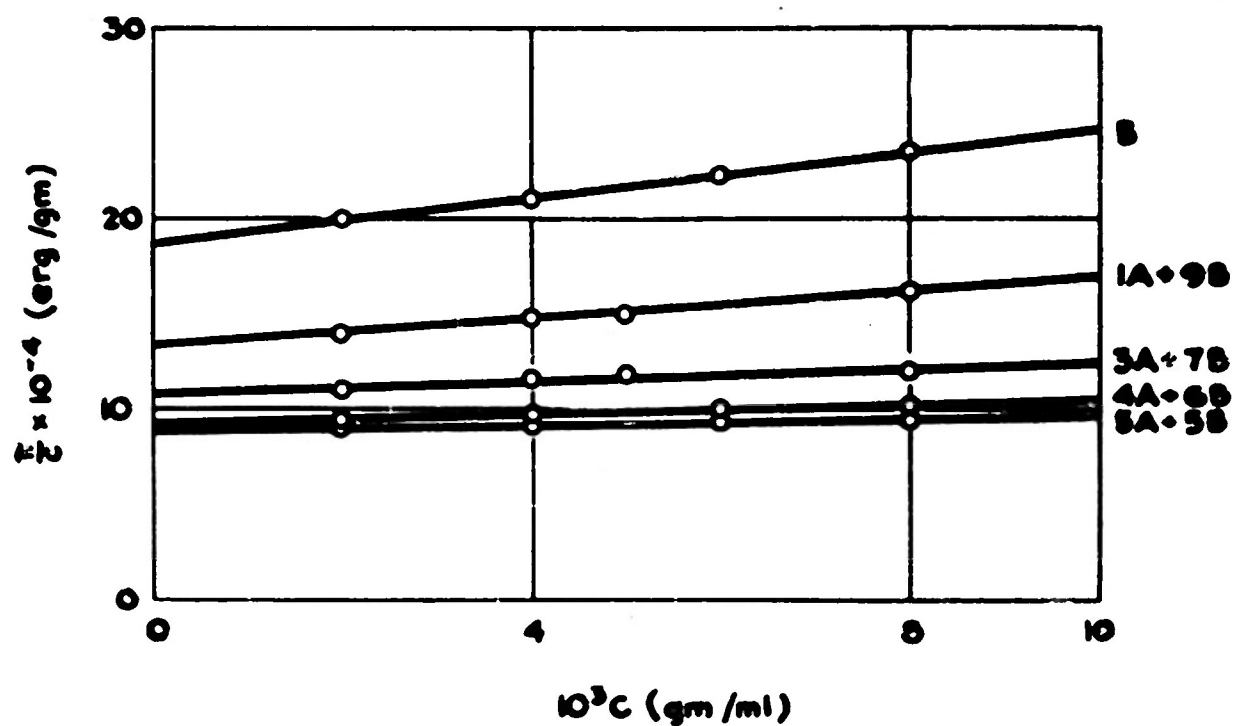
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FIG. 1



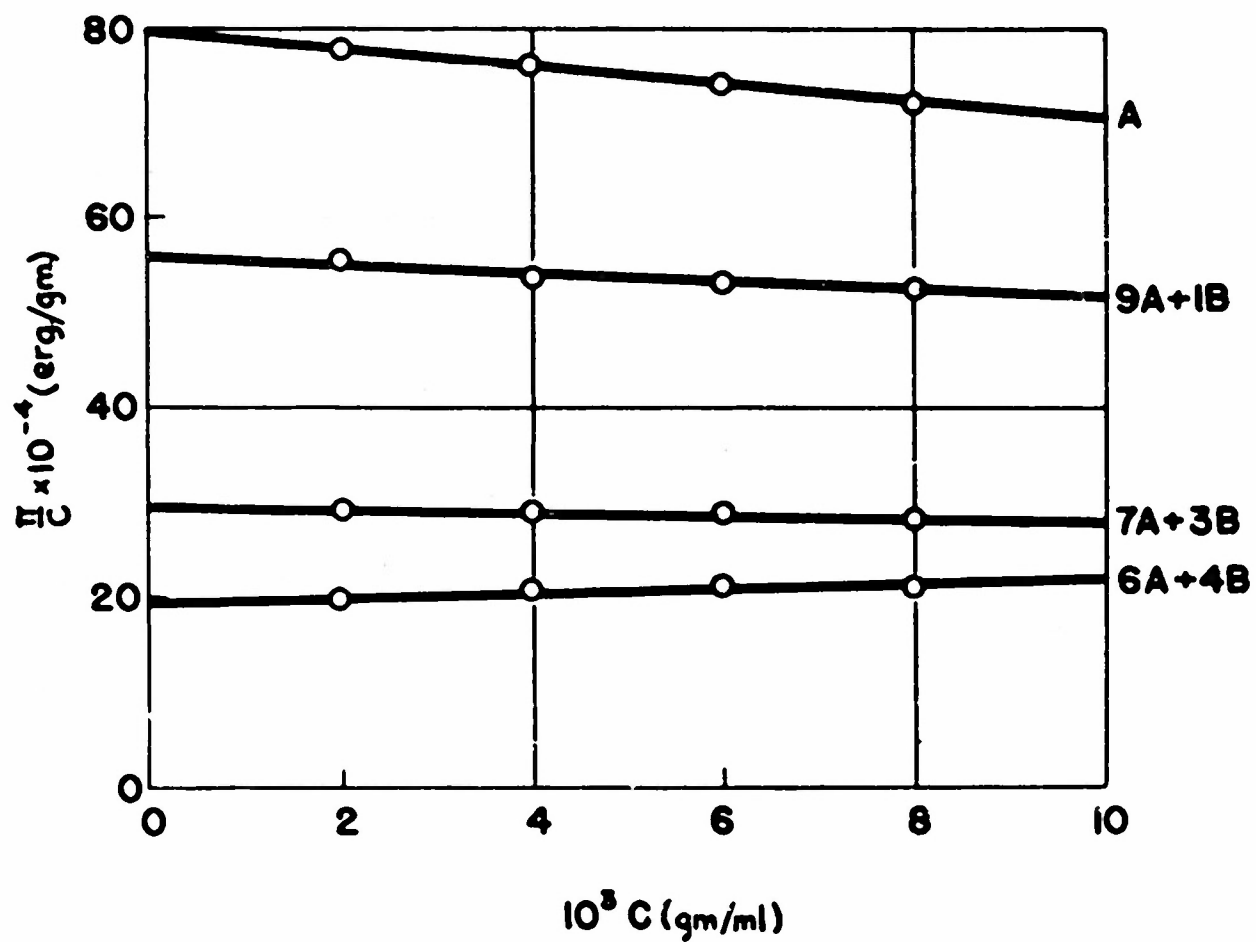
Reduced osmotic pressure plots of butanone solutions of acidic polymer (A) and mixtures of acidic and basic polymers (A + B). (Temp. 30.2°C.).

FIG. 2



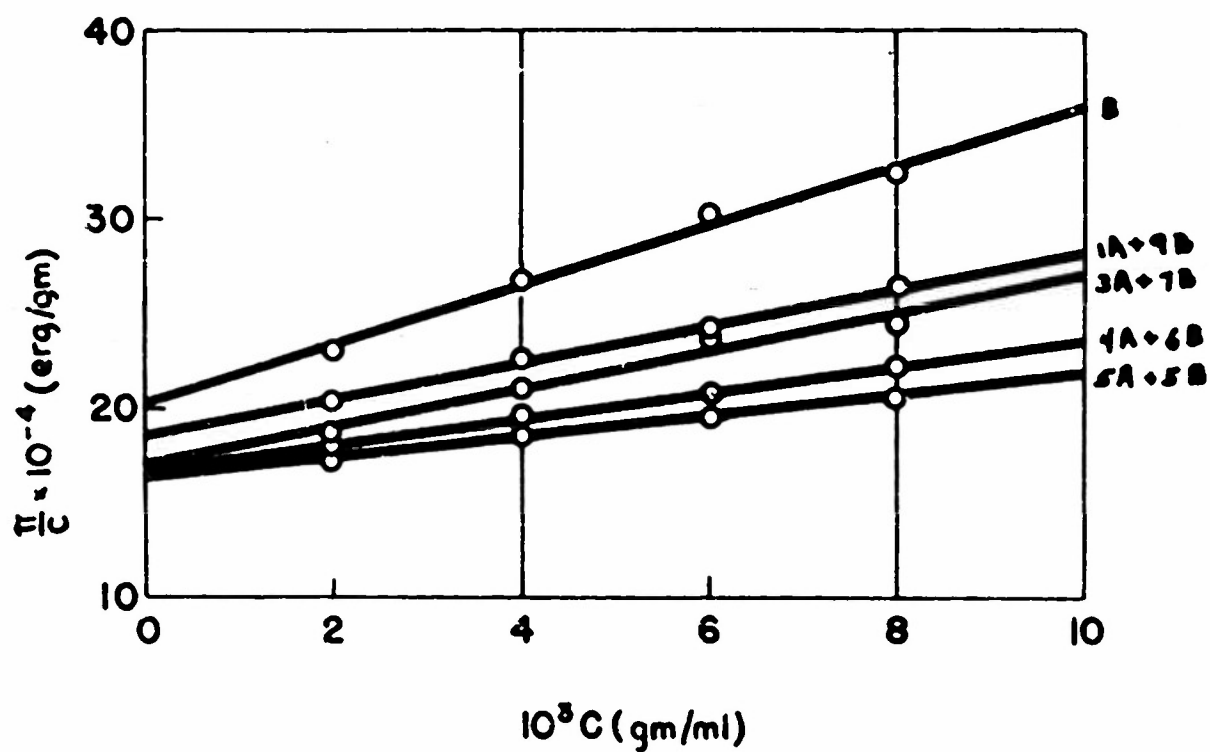
Reduced osmotic pressure plots of butanone solutions of basic polymer (B) and mixtures of acidic and basic polymers (A + B). (Temp. 30.2°C.).

FIG. 3



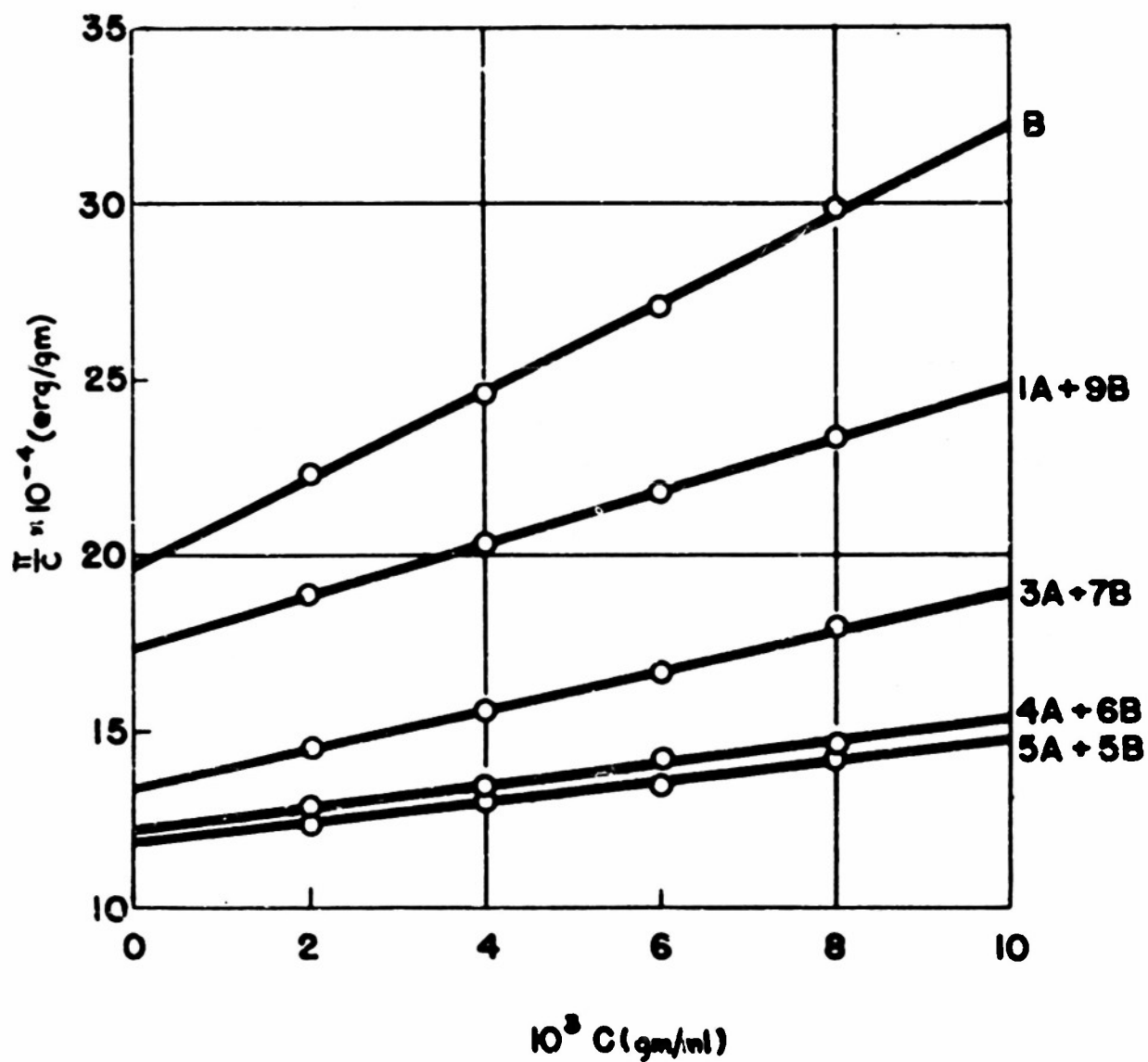
Reduced osmotic pressure plots of butanone solutions of acidic polymer (A) and mixtures of acidic and basic polymers (A + B). (Temp. 50.1°C.).

FIG. 4



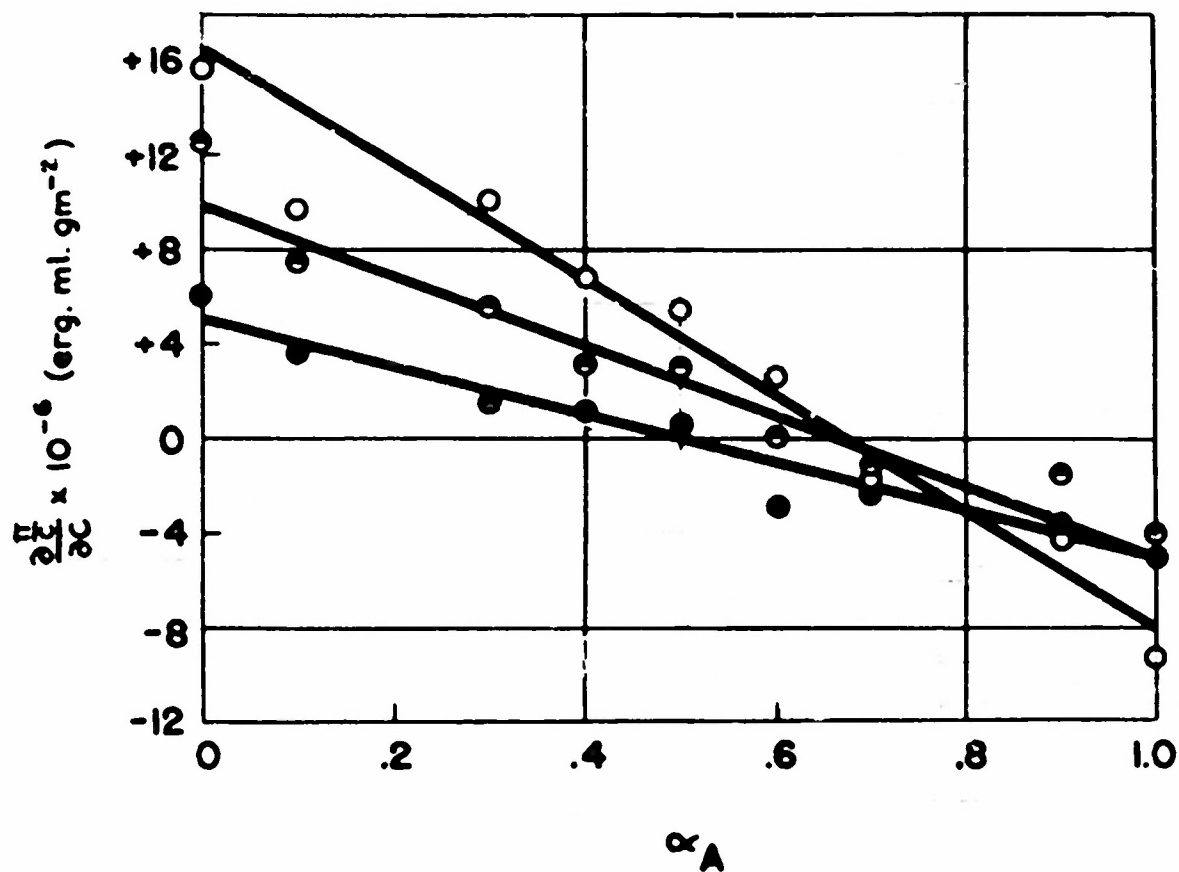
Reduced osmotic pressure plots of butanone solutions of basic polymer (B) and mixtures of acidic and basic polymers (A + B). (Temp. 50.1°C.).

FIG. 6



Reduced osmotic pressure plots of benzene solutions of basic polymer (B) and mixtures of acidic and basic polymers (A + B). (Temp. 49.7°C.).

FIG. 7



Slopes (Y) of reduced osmotic pressure plots of solutions of polymers (A) and (B) and their mixtures.
 • Butanone at 30.2°C. ○ Butanone at 50.1°C.
 • Benzene at 49.7°C.